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Three-Dimensional Supermolecules Assembled from a Tris(Zn^{2+}−cyclen) Complex and Di- and Trianionic Cyanuric Acid in Aqueous Solution (Cyclen = 1,4,7,10-Tetraazacyclododecane)

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Abstract: Two new three-dimensional supermolecules having closed hollow frameworks were isolated by self-assembly of a tris(Zn^{2+}−cyclen) (Zn_3L^3) (L^3 = 1,3,5-tris(1,4,7,10-tetraazacyclododecan-1-ylmethyl)benzene) with di- (CA^{2-}) or trideprotonated cyanuric acid (CA^{3-}) in aqueous solution (cyclen = 1,4,7,10-tetraazacyclododecane). One was a very stable 2:3 complex of Zn_3L^3 and CA^{2-} formed above pH 6, which was isolated from a 2:3 mixture of Zn_3L^3 and cyanuric acid (CA) in aqueous solution and characterized by ^1H NMR and potentiometric pH titration. The X-ray crystal structure showed that each CA^{2-} is sandwiched between two Zn^{2+}−cyclen moieties extended from two tris(Zn^{2+}−cyclen). The crystal data: formula $C_{75}H_{147}N_{36}O_{36}Cl_3Zn_6$ ($((Zn_3L^3)_2-(CA^{2-})_3\cdot 3NO_3\cdot 3ClO_4\cdot 6H_2O)$), $M_r = 2627.84$, monoclinic, space group $P2_1/n$ (No. 14), $a = 27.327(3)$ Å, $b = 29.127(2)$ Å, $c = 16.025(2)$ Å, $\beta = 90.56(1)°$, $V = 12754(1)$ Å^3, $Z = 4$, $R = 0.091$, and $R_w = 0.110$. The second one was an unexpected supramolecular complex by 4:4 self-assembly of Zn_3L^3 and CA^{3-}, which was isolated by allowing a 1:1 mixture of Zn_3L^3 and CA in aqueous solution to stand at pH 11.5. Its X-ray crystal analysis showed a highly symmetric 4:4 assembling complex having an inner hollow, which was schematically represented as a truncated tetrahedron made by binding four equilateral triangles and four scalene hexagons to each other through $CA^{3-}-Zn^{2+}$ bonds. Crystal data of the 4:4 supramolecular complex: formula $C_{144}H_{344}N_{72}O_{88}Zn_{12}$ ($((Zn_3L^3)_4-(CA^{3-})_4\cdot 12NO_3\cdot 40H_2O)$), $M_r = 5277.29$, cubic, space group $I\bar{4}3m$ (No. 217), $a = 23.430(4)$ Å, $V = 12862(3)$ Å^3, $Z = 2$, $R = 0.068$, and $R_w = 0.086$. The 2:3 supercomplex is stable in H_2O, while the 4:4 complex is stable only in solid or in DMSO solution and tends to go back to the 2:3 complex in the presence of H_2O. The 2:3 and 4:4 complexes were equivalent in terms of acid−base equilibrium, and direction of the disproportionation to the 4:4 complex was favored due to its insolubility.

Introduction

Highly organized nanoscale structures in viruses, enzymes, organelles, and cells are formed from a vast number of small and different components.[1] Self-assembly and spontaneous assembly of natural polymers such as nucleic acids, proteins, lipids, and carbohydrates through noncovalent bonds in solution, gel, and solid states are ubiquitous in nature. Artificial supramolecular architectures are often constructed from imide-containing molecules including nucleic acid bases and barbiturates. Typical driving forces for self-assembly of those molecules are hydrogen bond, aromatic $\pi-\pi$ stacking, van der Waals interaction, metal−ligand coordination, etc.[2−19] For example, Feibush et al. reported that *N*,*N*′-2,6-pyridinediylbis(alkanamide) receptor recognizes monoimide (e.g., thymidine (dT)) and diimide compounds to form complexes such as **1** stabilized by three hydrogen bonds, which made possible chiral separation of racemic imides by a receptor-bound HPLC column (Figure 1).[4] Dipyridine compound **3** designed by Hamilton's group[5] and metallomacrocycle by Reinhoudt's group[6] were effective receptors for barbiturates, a typical diimide drug. "Tennis balls" and "baseballs" reported

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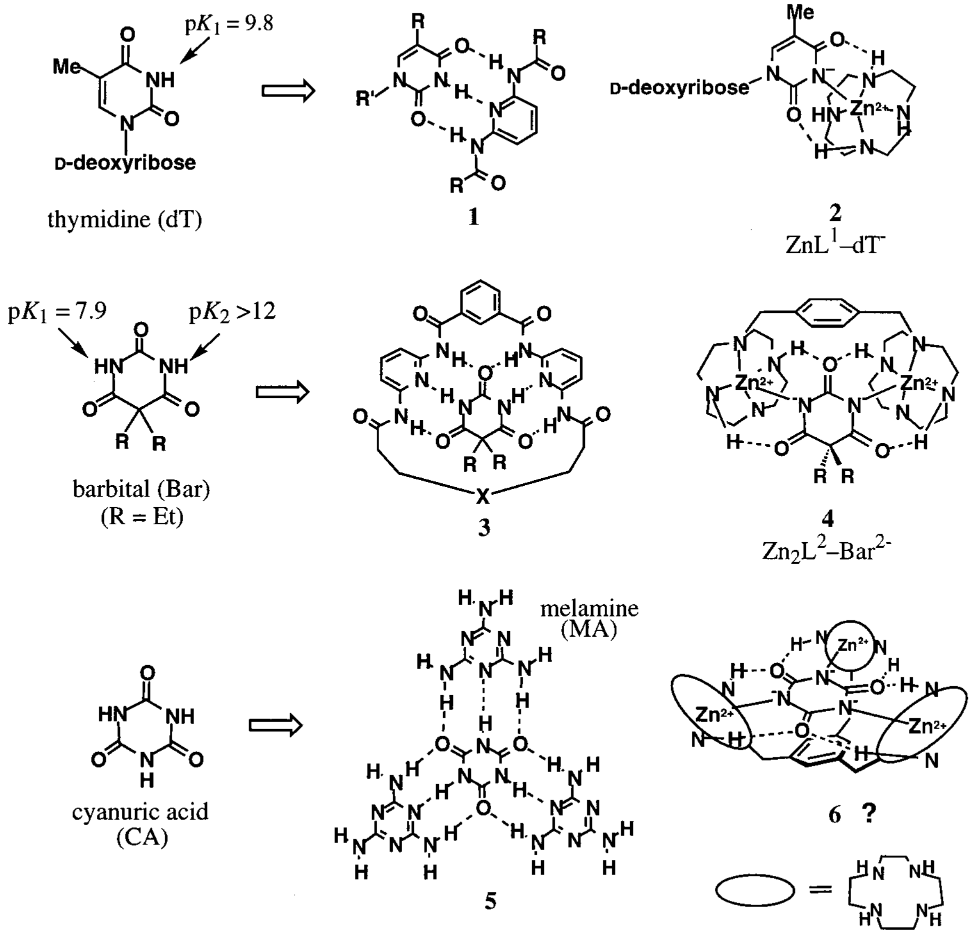

Figure 1. Molecular recognition of monoimide (thymine and uracil), diimide (barbiturates), and triimide (cyanuric acid) by organic and inorganic host molecules.

by Rebek et al. were molecular capsules by three-dimensional self-assembly of two glycouril compounds through hydrogen bonds.[7] For triimide molecules such as cyanuric acid (CA), Whitesides and co-workers reported a nanometer-scale self-assembly **5** with melamine (MA) forming supramolecular lattices and rosettes.[8] All of these supermolecules, however, are designed in hydrophobic environments. Development of new self-assembling molecules that are formed *in aqueous solution* is now acutely required.[8b]

Use of metal−ligand coordination bonds is an alternative methodology to build supramolecular complexes.[11−19] Recently emerging supermolecules include polynuclear palladium complexes designed by Fujita's[14] and Stang's groups,[15] which are generated by spontaneous self-assembly of Pd^{2+} or Pt^{2+} ions with poly(pyridyl) or phosphine ligands. Schwabacher et al. reported a cyclophane-like macrocycle formed by $metal^{2+}$−bis(amino acid) chelation as a self-assembling receptor having a hydrophobic cavity.[16] Atwood's group[17] has isolated a dinuclear copper(II)−macrotricyclic complex from water, and Raymond's group[18] synthesized supramolecular clusters in aqueous solution.[19]

Since 1981, we have been interested in molecular recognition of organic and inorganic anions in aqueous solution by macrocyclic polyamines and their metal complexes.[20−25] For recognition of monoimide compounds, we found that Zn^{2+}−cyclen (cyclen = 1,4,7,10-tetraazacyclododecane) complex **7** (ZnL^1) is a highly selective host for dT and U (uridine), whose

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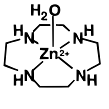
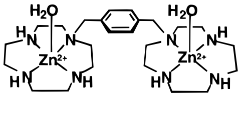
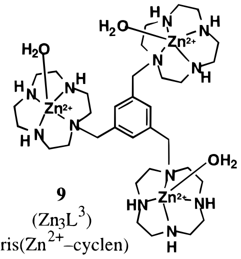
pK_1 values for the imide proton are 9.8 and 9.2, in neutral aqueous solution to yield the 1:1 complex **2** (ZnL^1-dT^- and ZnL^1-U^-), where the imide-deprotonated dT^- (or U^-) binds with a zinc(II) cation and two carbonyl oxygens bind with the two complementary cyclen NH's through hydrogen bonds.[21,22] The apparent affinity constant, log K_{app} ($K_{app} = [\mathbf{2}]/[\mathbf{7}_{free}][dT_{free}]$ (M^{-1})) in aqueous solution, is 3.1 at pH 7.6 and 25 °C with $I = 0.1$ ($NaNO_3$).[21a]



7
(ZnL^1)



8
(Zn_2L^2)

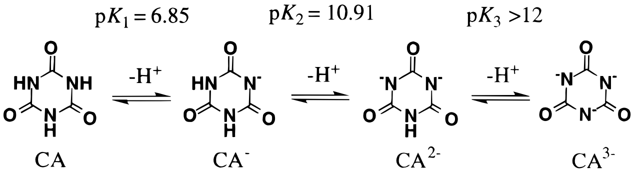


9
(Zn_3L^3)
tris(Zn^{2+}–cyclen)

For recognition of barbital (Bar), a diimide compound, we designed a dimeric Zn^{2+}–cyclen connected through a *p*-xylene unit, **8** (Zn_2L^2).[23] The first deprotonation constant for Bar $\leftrightarrows$ $Bar^- + H^+$, pK_1, is 7.9 and the second one for $Bar^- \leftrightarrows Bar^{2-} + H^+$, p$K_2$, is over 12, indicating that the second deprotonation would hardly occur at pH <12 in the absence of **8**. However, it was interesting to discover that an unexpected 2:2 supramolecular complex ($(Zn_2L^2)_2-(Bar^{2-})_2$) was isolated along with an anticipated 1:1 complex **4** ($Zn_2L^2-Bar^{2-}$), in which two imide N^- are bound to two zinc(II) cations of **8** and that the equilibrium exists between the two forms in aqueous solution.[23a]

Having obtained a trimeric (Zn^{2+}–cyclen) unit connected through 1,3,5-trimethylbenzene **9** (tris(Zn^{2+}–cyclen), Zn_3L^3) (L^3 = 1,3,5-tris(1,4,7,10-tetraazacyclododecan-1-ylmethyl)benzene),[24] we were interested to see whether some supermolecules containing three NH-deprotonated CA (CA^{3-}) such as **6** would be formed by self-assembly. In this paper, we present the discovery of novel supramolecular chemistry occurring between **9** and CA at various pH's in aqueous solution. One of the self-assembly products, a 4:4 complex of **9** and CA^{3-}, is a totally unexpected supermolecule, which is extremely interesting structurally, mechanistically, and as a new material.

Scheme 1

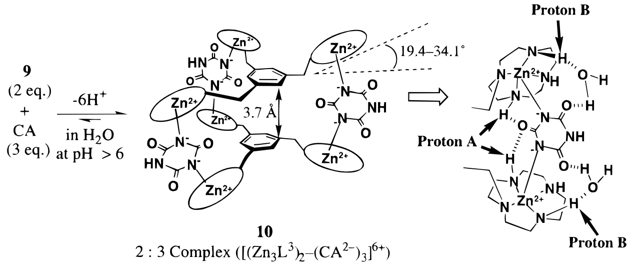


$$CA \rightleftarrows CA^- + H^+ : \quad K_1 = [CA^-]a_{H^+} / [CA] \qquad (1)$$

$$CA^- \rightleftarrows CA^{2-} + H^+ : \quad K_2 = [CA^{2-}]a_{H^+} / [CA^-] \qquad (2)$$

$$CA^{2-} \rightleftarrows CA^{3-} + H^+ : \quad K_3 = [CA^{3-}]a_{H^+} / [CA^{2-}] \qquad (3)$$

Scheme 2



10
2 : 3 Complex ($[(Zn_3L^3)_2-(CA^{2-})_3]^{6+}$)

Results and Discussion

Deprotonation of Cyanuric Acid. Although already reported,[26] the three deprotonation constants, pK_1, pK_2, and pK_3 defined by eqs 1–3 at 25 °C and $I = 0.1$ ($NaNO_3$) were determined for the present reaction conditions by potentiometric pH titration, which gave 6.85 ± 0.05, 10.91 ± 0.05, and >12, respectively (Scheme 1). The pK_3 value of >12 implies that the third deprotonation to give the trianionic form (CA^{3-}) would be extremely difficult in aqueous solution in the absence of **9**. Moreover, a molecular model study suggested that an initially anticipated 1:1 complex **6** in which all of the three carbonyl groups and three imide nitrogens of CA^{3-} and three zinc(II) cations in **9** are fixed on a plane may be sterically unfeasible. We then might better ponder other types of sterically and/or electronically feasible supercomplexes for the difficult deprotonation to take place.

Isolation and Characterization of the 2:3 Complex (10) from 9 and CA^{2-}. Fine colorless prisms (180 mg, 57% yield) were obtained when a mixture of $\mathbf{9}\cdot 6NO_3$ (300 mg, 0.24 mmol), CA (51 mg, 0.40 mmol), and $NaClO_4$ (50 mg, 0.41 mmol) in aqueous solution (10 mL, adjusted to pH 10 by NaOH) was slowly evaporated in vacuo. The elemental analysis (C, H, N) was consistent with the 2:3 complex of **9** and CA^{2-} plus $3ClO_4^-$, $3NO_3^-$, and $6H_2O$ ($C_{75}H_{147}N_{36}O_{36}Cl_3Zn_6$). The IR spectrum of the crystals showed absorbance peaks at 1597 and 1651 cm^{-1} (imide CON^-) and a weak peak at 1760 cm^{-1} (imide CONH), while CA exhibited absorbance peaks at 1779, 1751, and 1724 cm^{-1} corresponding to neutral imide moiety (**9** does not have a characteristic peak at 1700–1800 cm^{-1}).

An X-ray crystal structure analysis revealed a sandwichlike structure **10** of the supercomplex comprising two molecules of **9** and three molecules of CA^{2-}, as shown in Scheme 2 and Figure 2.

Panels a and b of Figure 2 are top and side views by stick and ball drawing and space-filling drawing, respectively. Each Zn^{2+}–cyclen unit in **10** has a distorted tetragonal-pyramidal

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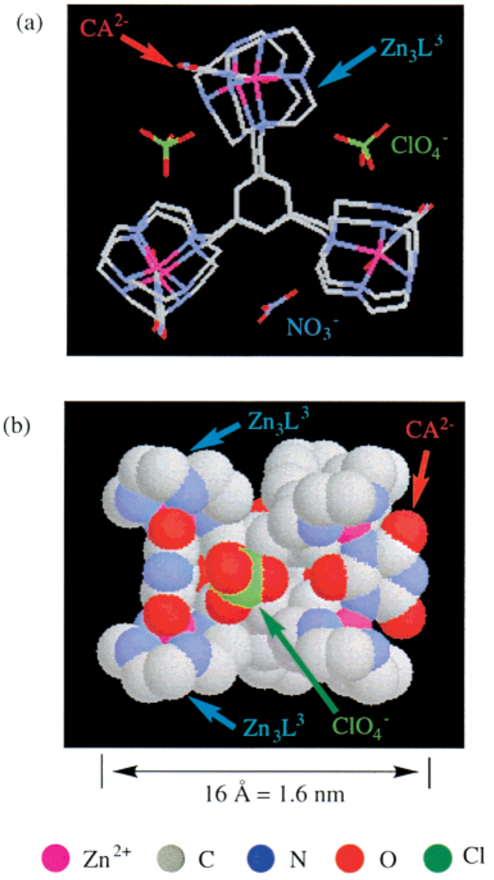

Figure 2. Stick drawing (a) and space-filling drawing (b) representing top and side views of the 2:3 supramolecular complex **10**, respectively, with anions (NO_3^- and ClO_4^-) in the grooves between CA^{2-} moieties. Purple, gray, blue, red, and green atoms are Zn^{2+}, C, N, O, and Cl, respectively. Other external anions, protons, and water molecules were omitted for clarity.

structure, and the zinc(II)−nitrogen bond lengths are 1.94−1.98 Å,[27] as found in the crystal structures of several Zn^{2+}−cyclen complexes.[21a,d,23−25] The two face-to-face Zn_3L^3 are almost superimposable (Figure 2a), and the phenyl groups of each **9** face each other with a distance of ~3.7 Å, which may permit $\pi-\pi$ stacking.[28] All the Zn^{2+}−cyclen units of Zn_3L^3 are spread out on the phenyl plane with three apical binding sites of each three zinc(II) located on the same face. The dihedral angles between benzene planes and cyclen planes are 19.4−34.1°, which indicates that three Zn^{2+}−cyclen units are twisted like a propeller to permit the $Zn^{2+}-N^-$ coordination bonds with two imide moieties of CA^{2-} (Scheme 2 and Figure 2b).

There are hydrogen bonds between the carbonyl oxygens of CA^{2-} and secondary amine protons of Zn_3L^3. The distances between nitrogen atoms on the cyclen rings and carbonyl oxygens of CA are 2.83−3.29 Å. Typical crystal parameters for **10** are listed in Table 1.[29]

Potentiometric pH Titration of the 2:3 Complex 10. We then performed potentiometric pH titration of the 2:3 Zn_3L^3−CA solution ($[Zn_3L^3] = 1$ mM) at 25 °C with $I = 0.1$ ($NaNO_3$) (Figure 3). It is evident that the 2:3 complex **10** was quantitatively formed above pH 6. The second deprotonation from CA (otherwise $pK_2 = 10.9$) was thus facilitated by the Zn^{2+} coordination. The complexation equilibria were assumed to be represented by eqs 4−7 and 11−14.

$$Zn_3L^3(H_2O)_3\ (\mathbf{9}) \rightleftarrows Zn_3L^3(H_2O)_2(HO^-) + H^+:$$

$$K_4 = [Zn_3L^3(H_2O)_2(HO^-)]a_{H^+}/[Zn_3L^3(H_2O)_3] \qquad (4)$$

$$Zn_3L^3(H_2O)_2(HO^-) \rightleftarrows Zn_3L^3(H_2O)(HO^-)_2 + H^+:$$

$$K_5 = [Zn_3L^3(H_2O)(HO^-)_2]a_{H^+}/[Zn_3L^3(H_2O)_2(HO^-)] \qquad (5)$$

$$Zn_3L^3(H_2O)(HO^-)_2 \rightleftarrows Zn_3L^3(HO^-)_3 + H^+:$$

$$K_6 = [Zn_3L^3(HO^-)_3]a_{H^+}/[Zn_3L^3(H_2O)(HO^-)_2] \qquad (6)$$

$$2(Zn_3L^3(H_2O)_3) + 3(CA^{2-}) \rightleftarrows [(Zn_3L^3)_2-(CA^{2-})_3]^{6+}\ (\mathbf{10}):$$

$$K_7 = [\mathbf{10}]/[\mathbf{9}]^2[CA^{2-}]^3 \qquad (M^{-4}) \qquad (7)$$

$$\mathbf{10} \rightleftarrows \mathbf{11} + H^+: \quad K_8 = [\mathbf{11}]a_{H^+}/[\mathbf{10}] \qquad (8)$$

$$\mathbf{11} \rightleftarrows \mathbf{12} + H^+: \quad K_9 = [\mathbf{12}]a_{H^+}/[\mathbf{11}] \qquad (9)$$

$$\mathbf{12} \rightleftarrows \mathbf{13} + H^+: \quad K_{10} = [\mathbf{13}]a_{H^+}/[\mathbf{12}] \qquad (10)$$

$$K_{app} = [(Zn_3L^3)_2-(CA^{2-})_m-(CA^{3-})_n]/ [\text{uncomplexed } Zn_3L^3]^2[\text{uncomplexed CA}]^3$$

$$(m, n = 0, 1, 2, 3, m + n = 3) \qquad (M^{-4}) \qquad (11)$$

$$[(Zn_3L^3)_2-(CA^{2-})_m-(CA^{3-})_n] = [\mathbf{10}] + [\mathbf{11}] + [\mathbf{12}] \qquad (12)$$

$$[\text{uncomplexed } Zn_3L^3] = [\mathbf{9}]_{free} + [Zn_3L^3(H_2O)_2(HO^-)]_{free} + [Zn_3L^3(H_2O)(HO^-)_2]_{free} + [Zn_3L^3(HO^-)_3]_{free} \qquad (13)$$

$$[\text{uncomplexed CA}] = [CA]_{free} + [CA^-]_{free} + [CA^{2-}]_{free} \qquad (14)$$

The deprotonation constants of three Zn^{2+}-bound waters in **9** defined by eqs 4−6, pK_4, pK_5, and pK_6, are 6.1, 7.3, and 8.6, respectively.[24] Analysis of the pH titration curves by the program BEST[30] was in good agreement with this 2:3 complexation scheme. Figure 4 shows the distribution diagram of six species ($Zn_3L^3(H_2O)_3$ (**9**) $Zn_3L^3(H_2O)_2(HO^-)$, CA^-, $[(Zn_3L^3)_2-(CA^{2-})_3]^{6+}$ (**10**), $[(Zn_3L^3)_2-(CA^{2-})_2-(CA^{3-})]^{5+}$ (**11**), and $[(Zn_3L^3)_2-(CA^{2-})-(CA^{3-})_2]^{4+}$ (**12**)) for a 1 mM **9**/1.5 mM CA mixture as a function of pH at 25 °C with $I = 0.1$ ($NaNO_3$) (for the structure of **11** and **12**; see Scheme 3). The population of the 2:3 complex **10** increased as pH was raised above 5 and reached nearly quantitative 49% (indicated with a bold line in Figure

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[27] The $Zn^{2+}-N^-$ length in **10** is shorter than the corresponding coordination bonds between metal cation and imide N^- in $Mn^{2+}-CA^-$ (2.28 Å), $Co^{2+}-CA^-$ (2.18 Å), and $Ni^{2+}-CA^-$ (2.14 Å): Falvello, L. R.; Pascual, I.; Tomás, M. *Inorg. Chim. Acta* **1995**, *229*, 135−142.

[28] UV spectrophotometric titration and isothermal titration calorimetry in aqueous solution of **9** and CA supported 2:3 complexation at pH 6−11. The ϵ value of **9** at 265 nm decreased by ~20% (from 3.0×10^2 to 2.4×10^2 ($M^{-1}\cdot cm^{-1}$)) on addition of 1.5 equiv of CA with an isosbestic point at 274 nm, possibly by a hypochromic effect due to $\pi-\pi$ stacking between the two benzene rings.

[29] For the Crystal Information Files (CIFs) for the X-ray crystal structure analysis of **10** and **15**, see Supporting Information.

[30] (a) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*, 2nd ed.; VCH: New York, 1992. (b) Martell, A. E.; Hancock, R. D. *Metal Complexes in Aqueous Solutions*.; Plenum Press: New York, 1996.

Table 1. Typical Parameters of X-ray Crystal Structure Analysis of the 2:3 Zn_3L^3−CA^{2-} Complex (**10**) and the 4:4 Zn_3L^3−CA^{3-} Complex (**15**)[a]

	10	**15**
formula	$C_{75}H_{147}N_{36}O_{36}Cl_3Zn_6$	$C_{144}H_{344}N_{72}O_{88}Zn_{12}$
M_r	2627.84	5277.29
cryst syst	monoclinic	cubic
space group	$P2_1/n$ (No. 14)	$I\bar{4}3m$ (No. 217)
a (Å)	27.327(3)	23.430(4)
b (Å)	29.127(2)	
c (Å)	16.025(2)	
β (deg)	90.56(1)	
V (Å^3)	12754(1)	12862(3)
Z	4	2
D_{calc} (g·cm^{-3})	1.368	1.362
μ (Mo Kα) (cm^{-1}	12.6	11.8
$2\theta_{max}$	50.6	54.8
R	0.091	0.068
R_w	0.110	0.086
no. of reflctns used for least squares ($I > 3\sigma(I)$)	7240	1004
no. of variables	773	76

[a] The structure were solved by direct methods (SIR 92) and refined by full matrix least squares.

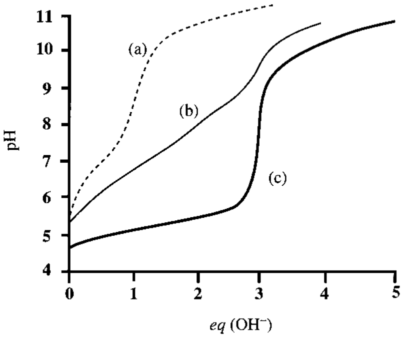


Figure 3. Typical titration curves of 1.0 mM CA (a), 1.0 mM **9** (b), and 1.5 mM CA + 1.0 mM **9** (c) with $I = 0.10$ ($NaNO_3$) at 25 °C. *eq* (OH^-) is the number of equivalents of base added.

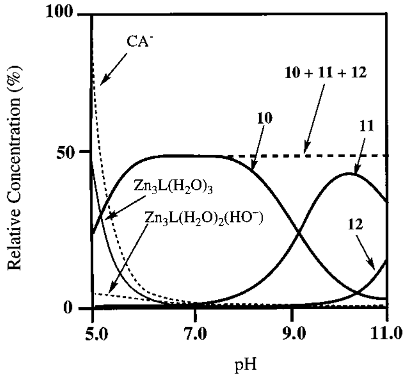
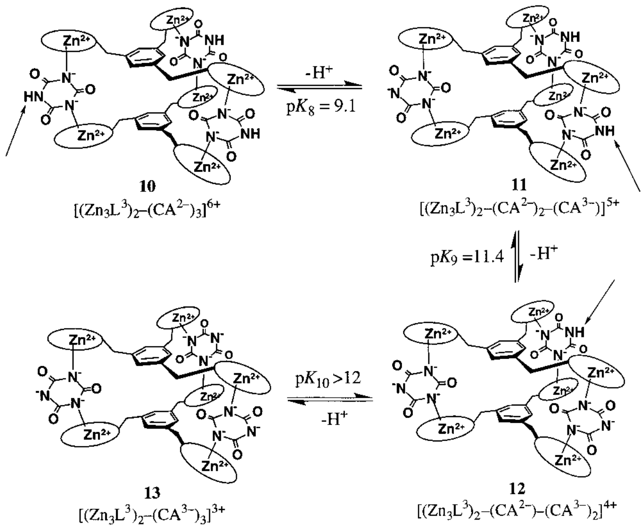


Figure 4. Distribution diagram for the **9** and CA species in a 1 mM **9**/1.5 mM CA mixture as a function of pH at 25 °C with $I = 0.10$ ($NaNO_3$). Vertical axis is a relative concentration of each species against a total amount of **9**. For clarity, species at less than 5% were omitted.

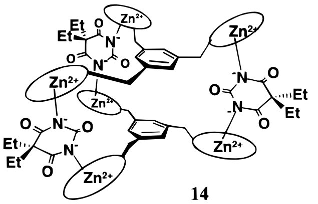
Scheme 3



4) at pH 6 (i.e., over 98% of **9** was converted into **10**). Apparent complexation constant, log K_{app} (defined by eqs 11−14), at pH 8.0, 9.0, 10.0, and 11.0 were 24.4, 25.4, 25.6 and 24.6, respectively.

By further analysis of the pH titration data at pH >8, we determined pK_a values for the remaining imide hydrogens in **10**, pK_8 (for **10** $\rightleftarrows$ **11**) = 9.1 ± 0.1, pK_9 (for **11** $\rightleftarrows$ **12**) = 11.4 ± 0.1, and pK_{10} (for **12** $\rightleftarrows$ **13**) >12, respectively, implying that two of the three CA^{2-} could be deprotonated at pH <12 (Scheme 3 and eqs 8−10). The sum of [**10**], [**11**], and [**12**] (indicated with a bold dashed line in Figure 4) is over 49% at pH 6−11.

For comparison, the complexation of **9** with barbital was examined by the potentiometric pH titration (with $I = 0.1$ ($NaNO_3$) at 25 °C).[31] These experiments strongly indicated that **9** and barbital also form a 2:3 complex, whose structure is most likely **14** ($(Zn_3L^3)_2$−$(Bar^{2-})_3$) in analogy to the structure of **10**.



14
$[(Zn_3L^3)_2-(Bar^{2-})_3]^{6+}$

$$K_{app} = [(Zn_3L^3)_2-(Bar^{2-})_3]/[\text{uncomplexed } Zn_3L^3]^2\,[\text{uncomplexed Bar}]^3\ (M^{-4}) \tag{15}$$

$$[\text{uncomplexed Bar}] = [\text{Bar}]_{free} + [\text{Bar}^-]_{free} \tag{16}$$

The log K_{app} for the 2:3 complexation of **9** and Bar (defined by eqs 13, 15, and 16) at pH 8.0, 9.0, 10.0, and 11.0 are 21.2, 19.7, 17.0, and 14.0, respectively, at 25 °C.

^{1}H NMR Study of the 2:3 Complex 10. Parts a and b of Figure 5 show the aromatic three protons (Ar*H*, all equivalent) of the ^{1}H NMR spectrum of **9** (1 mM) and isolated **10** (0.5 mM), respectively, in D_2O at pD 8.0 ± 0.1 and 35 °C. In comparison with Ar*H* of **9**, the Ar*H* of **10** considerably shifted upfield, possibly due to π−π stacking (see Figure 2). Upon mixing **9** with 1.5 equiv of CA at pD 8.0, a spectrum indentical to Figure 5b was obtained, supporting that **10** is quantitatively formed at millimolar concentration.[32,33] However, the ^{1}H NMR spectrum of a 1:1 mixture of **9** and CA at pD 8.0 showed (Figure 5c), in addition to the peak for unreacted **9**, an unidentified peak

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[31] The pK_a values of two imide protons of barbital were reported to be 7.85 and >12, respectively.[23]

[32] For comparison, ^{1}H NMR spectra of a dimeric (Zn^{2+}−cyclen) having an *m*-xylene spacer (Zn_2L^4)[21g,23b,24] with CA in D_2O exhibited complicated peaks with small upfield shifts, implying that the dimeric zinc(II) complex may also assemble with CA, but without distinct structures.

[33] The ^{1}H NMR spectra of **10** showed negligible pD dependency at pD 6.0−11.0 and negligible temperature dependency in the range of 25−85 °C.

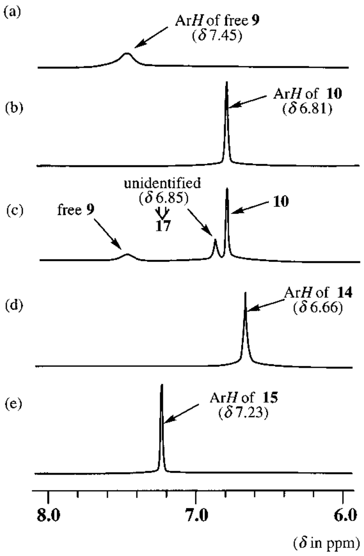


Figure 5. Aromatic regions (Ar*H*) of ^{1}H NMR spectra, 35 °C: (a) free **9** (1.0 mM) in D_2O, (b) **10** (0.5 mM) in D_2O, (c) **9** (1.0 mM) + CA (1.0 mM) in D_2O, (d) **9** (1 mM) + Bar (1.5 mM) in D_2O, and (e) **15** (0.5 mM) in DMSO-d_6. The pD values of (a−d) were 8.0 ± 0.1.

at δ 6.85 (in the following discussion, this peak was assigned to the 2:2 **9**−CA complex **17**).

For comparison, we measured the ^{1}H NMR of **9** (2 mM) in the presence of Bar (3 mM) in D_2O at pD 8.0 and 35 °C (Figure 5d), showing a singlet of Ar*H* at δ 6.66 to support a quantitative formation of **14**.

The ^{1}H NMR spectrum of **10** in D_2O suggested very stable hydrogen bonds between the cyclen N*H*'s and carbonyl oxygens of CA^{2-} in **9**. The protons A or B in Scheme 2 did not exchange with D of D_2O even after 2 days. They underwent complete H−D exchange only after ultrasonification for over 48 h. The X-ray structure analysis revealed indirect hydrogen-bonding NH's (proton B) as well as direct hydrogen bonds (proton A). A similar direct hydrogen bond and an indirect hydrogen bond were seen between Zn^{2+}−cyclen **7** and *N*-methylthymine.[21a]

A Novel 4:4 Complex (15) of 9 and CA^{3-} from Alkaline Aqueous Solution. Slow evaporation over a week of an aqueous solution (8 mL, adjusted to pH 11.5 by NaOH) of $\mathbf{9}\cdot NO_3^-$ (94 mg, 0.07 mmol) and CA (9 mg, 0.07 mmol) yielded fine colorless prisms (73 mg, 77% yield), whose elemental analysis (C, H, N) was consistent with a 1:1 stoichiometry of **9** and CA^{3-} with $3NO_3^-$ and $10H_2O$ ($C_{36}H_{86}N_{18}O_{22}Zn_3$). The new complex was soluble only in DMSO-d_6 and unstable in H_2O (see following discussion). Its ^{1}H NMR spectra in DMSO-d_6 showed a singlet at δ 7.23 for the Ar*H* (Figure 5e), which shifted a little upfield with respect to Ar*H* for **9** (δ 7.42 in DMSO-d_6) and downfield compared to Ar*H* for **10** (δ 6.73 in DMSO-d_6/D_2O (1:1 (v/v)).

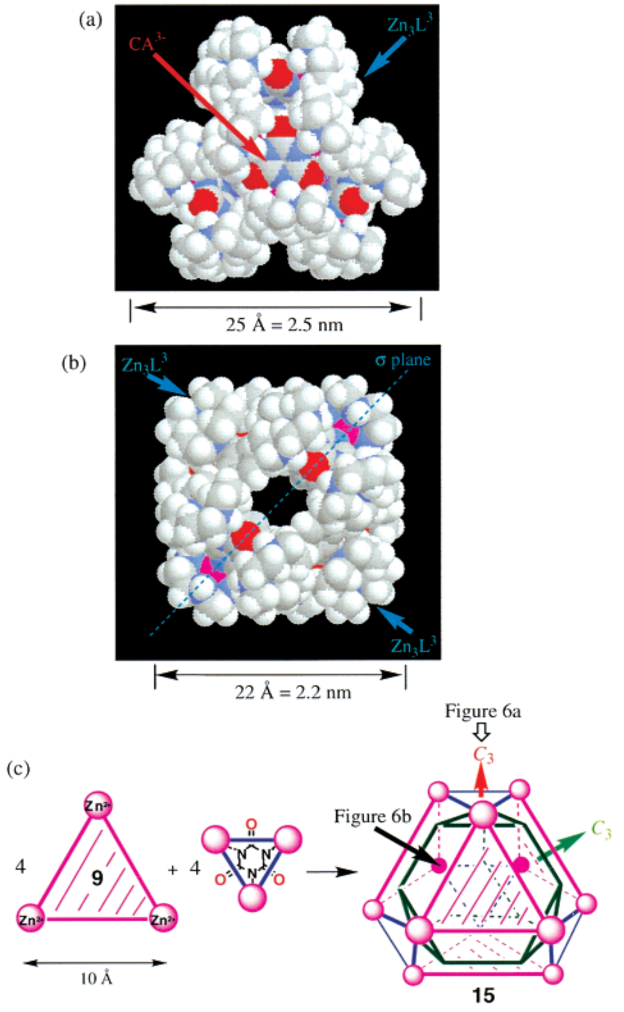
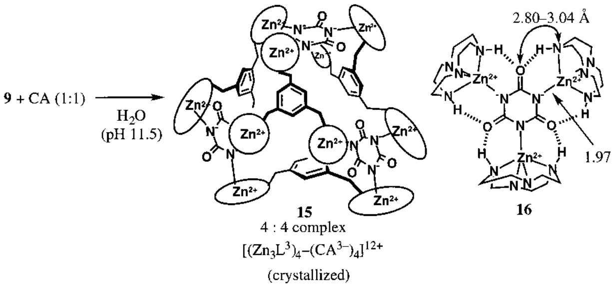


Figure 6. Space-filling drawings of the supramolecular cage **15** by 4:4 self-assembly of **9** and CA^{3-} viewed (indicated by a bold black arrow in (c)) along a σ symmetry plane (a light blue dashed line in (b)) (a) and viewed (indicated by a bold open arrow in (c)) along a red C_3 symmetry axis (b), respectively. Purple, gray, blue, red, and white atoms are Zn^{2+}, C, N, O, and H, respectively. All protons were added by calculation using the program teXsan, and all NO_3^- and H_2O were omitted. In (c), the structure of **15** is schematically illustrated as a purple cuboctahedral framework made of four molecules of **9** (purple equilateral triangles) and four CA^{3-} parts (blue equilateral triangles). A green framework is the inner cavity of **15**, as presented by a truncated tetrahedron (see also Figure 7). Red and light green arrows indicate two C_3 symmetry axes.

Scheme 4



To our astonishment, its single-crystal X-ray diffraction analysis disclosed a novel cage structure **15**, which is *an assembly of four **9** and four CA^{3-}* (Scheme 4). This is the first example of the trianionic CA form in aqueous solution (see **17**). The four molecules of **9** constructed four tetrahedral faces and four molecules of CA^{3-} linked them at four edges (Figure 6). The space group of **15** is $I\bar{4}3m$ (No. 217), implying a highly symmetric (S_3) structure with two C_3 symmetry axes presented by red and light green arrows in Figure 2e (four axes for each C_3 symmetry) and four σ symmetry (mirror reflection) planes. A view (a bold open arrow in Figure 6c) along one of the C_3 symmetry axes shows a triangle framework of **15** (the external size in this view is ~2.5 nm), where one of the CA^{3-} is located in the center (Figure 6a). Another view (a bold black arrow in Figure 6c) along a σ symmetry plane (a light blue dashed line) shows **15** as a cagelike supermolecule having a cubic shape and a nanometer-scale hollow (the external size is ~2.2 nm) (Figure 6b). In Figure 6c, **9** is represented by a purple equilateral

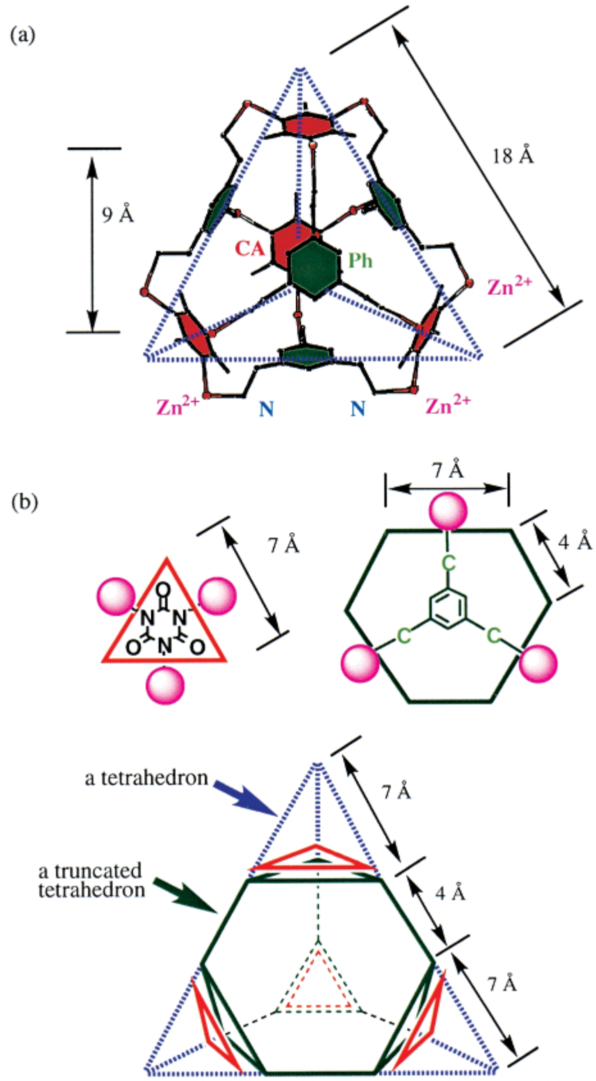
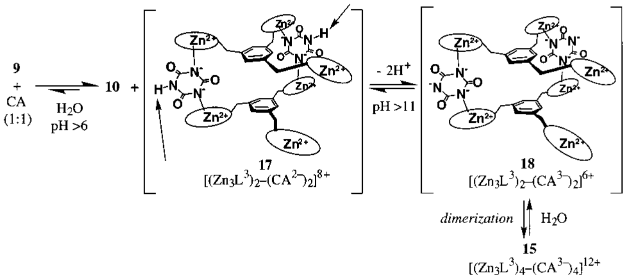


Figure 7. (a) Representation of the inner space of the supramolecular cage **15**. For clarity, cyclen rings were omitted. Inner distance between a phenyl group and a CA^{3-} is ~9 Å. (b) Schematic representation of the inner space of **15** having a truncated tetrahedron shape. The dashed blue lines indicate a tetrahedron (~18 Å side), from which four small tetrahedrons (~7 Å side) at four tops are cut off by four red triangles including CA^{3-}, whose three imide N^-'s are coordinated to zinc(II) cations. A green scalene hexagon represents an interior face including a benzene ring of Zn_3L^3.

triangle having three Zn^{2+} ions (purple circles) at each edge and the CA^{3-} part is represented by a blue triangle. Self-assembly of 4 purple triangles and 4 blue triangles through 12 coordination bonds gives **15**, whose structure is schematically represented as a purple cuboctahedral framework.

As shown in **16**, the superstructure of **15** was reinforced by the hydrogen-bonding network between N−H···O═C of CA^{3-} (24 hydrogen bonds in total). The average length of the coordination bonds between imide anion and zinc(II) cation is 1.97 Å, and the hydrogen bond lengths between nitrogen atoms on cyclen rings and carbonyl oxygens are 2.80−3.04 Å.[34] The intermolecular interactions between each **15** molecule in the crystal were not seen. The crystal data are listed in Table 1.[29,35]

Scheme 5



It is noteworthy that **15** has a well-defined inner space, which is separated from the outer space by four phenyl groups and four CA^{3-} (Figure 7a). For better understanding, its inner cavity structure may be visualized as a three-dimensional truncated tetrahedron (Figure 7), which is made by cutting four small regular tetrahedrons (~7 Å side) off by four red equilateral triangles including CA^{3-} at the four apexes of the large regular tetrahedron drawn with dashed blue lines (~18 Å side). This shape is composed of four equilateral triangles and four scalene hexagons including a benzene ring of Zn_3L^3. The short edges of 4 Å are positioned at the entrance to the inner cavity. The approximate internal volume of this hollow is ~140 Å^3.[36] In Figure 6c, the green interior framework is drawn in the purple exterior skeleton of **15**.

Study for Equilibrium between 10 and 15 in Solution. To elucidate the occurrence of **15** in aqueous solution, we measured its ^1H NMR spectrum. Although the 4:4 complex **15** was stable in fresh DMSO-d_6 solution (Figure 5e), it slowly decomposed. In D_2O at pD 8.0, **15** only initially gave a broad singlet peak at the same δ 7.2, which immediately disappeared to give the same spectrum as Figure 5c, indicating that **15** was immediately disproportionated into **10**, **9**, and an unidentified species in aqueous solution (the ratio of [**9**]:[**9** in **10**]:[**9** in an unidentified species (**17**)] was 27:53:20 at pD 8.0).[37] Addition of D_2O into a DMSO-d_6 solution of **15** yielded the same spectrum.

We provisionally assigned the unknown species at δ 6.85 (under the condition of [**9**] = [CA], Figure 5c) to a 2:2 complex **17**, in which two CA^{2-} molecules are sandwiched by zinc(II) cations, as a likely intermediate linking **15** with **9** (Scheme 5). As suggested by the pK_8 of 9.1 and pK_9 of 11.4 for the equilibrium of **10** $\rightleftarrows$ **11** $\rightleftarrows$ **12**, the double deprotonation from the remaining imide N*H* in CA^{2-} of **17** to yield **18** would likely occur at pH >11. Then, the 4:4 complex **15** is a product from dimerization of **18**. Since **10**, **15**, and **18** are all equivalent in acid−base neutralization (i.e., six deprotonations), these species might have been indistinguishable by the 1:1 **9**/CA pH titration.

On the basis of the combined potentiometric pH titration and NMR studies, the reaction of **9** → **10** → **15** may be summarized in Scheme 6. At millimolar-order concentration in water, the 2:3 supramolecular complex **10**, which is kinetically and thermodynamically stable, is formed as an exclusive species at pH >6 through a hypothetical intermediate **17**. By combining the K_{app} value of 24.4 for the 2:3 complexation of **9** and CA (eq 11) at pH 8.0 and the ratio of **10** and **17** (53:20) determined by ^1H NMR at pD 8.0 (Figure 5c), we estimated the log K_{app}'

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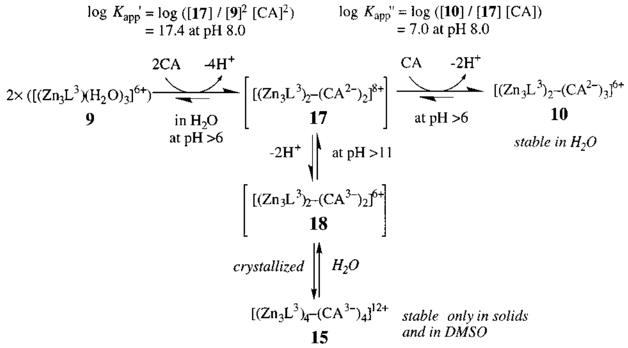
[34] The distance between amine atoms on MA and oxygen atoms on CA in **5** is 2.94 Å, and the distance between amine atoms on 1,3,5-triazine ring of MA and imide nitrogens of CA is 2.86 Å: Wang, B., Y.; Wei, B.; Wang, Q. *J. Crystallogr. Spectrosc. Res.* **1990**, *20*, 79−84.

[35] We could not observe mass peaks or fragmentations corresponding to **10** and **15** in electron ionization (EI), fast atom bombardment (FAB), electron spray ionization (ESI), and time-of-flight (TOF) mass spectrometric experiments.

[36] Six molecules of H_2O and four NO^{3-} were found in the inner cavity of **15**.

[37] The theoretical ratio of [**9**], [**9** in **10**], and [**9** in **17** (see following discussion in the text)] should be 0.25:0.5:0.25, if **15** is equally degraded into **9**, **10**, and **17**, which almost fit to the observed NMR results.

Scheme 6



value for the formation of **17** (defined by eqs 17, 13, and 14)

$$K_{app}' = [(Zn_3L^3)_2{-}(CA^{2-})_2\ (\mathbf{17})]/$$
$$[\text{uncomplexed } Zn_3L^3]^2\,[\text{uncomplexed CA}]^2 \qquad (M^{-3}) \quad (17)$$

$$K_{app}'' = [\mathbf{10}]/[\mathbf{17}]\,[\text{uncomplexed CA}] =$$
$$K_{app}/K_{app}' \qquad (M^{-1}) \quad (18)$$

to be 17.4 at pH 8.0. Thus, the log K_{app}'' value for the complexation of **17** and CA to yield **10** (by eq 18) is 7.0. These values imply that the 2:2 complex **17** would quantitatively trap a free CA (to **10**) at millimolar-order concentration.

Although the possible intermediate **17** (+ **18**) existed only in 15−20% at pD 11.0 and [**9**] = [CA] = 1−4 mM, the 4:4 supercomplex **15** crystallized in 77% yields from a 1:1 mixture of **9** and CA. We presume that this is due to its much lower solubility in water than other species. The 4:4 complex is appreciably stable in DMSO, but not in the presence of H_2O.[38] The formation of **15** containing CA^{3-} in H_2O might be compensated for by the crystal packing force and favorable hydrogen bond formation in the solid state.[39] However, dissolved in H_2O, this hydrogen bond network should be destroyed to be disproportionated into **9**, **10**, and **17**.

Conclusions

A 2:3 mixture of tris(Zn^{2+}−cyclen) **9** and cyanuric acid self-assemble in aqueous solution (pH >6) to quantitatively form a sandwichlike 2:3 supramolecular complex **10**, which was isolated and fully characterized by potentiometric pH titration, ^{1}H NMR, and X-ray crystal analysis. Another self-assembling capsule supercomplex was crystallized from a 1:1 mixture of **9** and CA in aqueous solution (at pH 11.5) in 77% yield. Its X-ray crystal analysis revealed a novel 4:4 cage **15** having a highly symmetric structure. Interestingly, the complexes **10** and **15** are equivalent in acid−base terms at higher pH and hence should be indistinguishable in the potentiometric pH titration. Because of its highly H_2O-insoluble properties, the formation of **15** as solid was facilitated and therefore the equilibrium was shifted from **10** via a provisionally assigned intermediate **17** (plus **18**) to **15**. The 24 hydrogen bonds may greatly contribute to the stability of **15**. The isolated **15** was only soluble in DMSO, where it was appreciably stable, as shown by the ^{1}H NMR study. However, addition of H_2O rapidly destroyed it, giving back **10**, **9**, and **17**.

A multiple recognition of anionic guests by macrocyclic zinc(II) complexes gives kinetically and thermodynamically stable supramolecular complexes.[21g,h] These findings should give an indispensable principle to design a new stable noncovalent architecture in aqueous solution. Cyanuric acid is a popular component for the “two- and three-dimensional” construction of nanometer-scale supermolecules in organic solution, probably because of its rigidity and bifunctionality as hydrogen bond donor and acceptor. In aqueous solution, pK_a values of acidic molecules as well as hydrogen-bonding nature are important. Construction of further three-dimensional architecture of nanometer scale may be achieved by multiple Zn^{2+}−cyclen units and molecules having multiple acidic moieties such as CA.[40]

Experimental Section

General Information. Melting points were determined by using a Yanaco melting point microapparatus without any corrections. All reagents and solvents used were of the highest commercial quality and used without further purification. Tris(Zn^{2+}−cyclen) (Zn_3L^3) complex **9** was synthesized as described previously.[24] Cyanuric acid was recrystallized from hot water, dried in vacuo, and confirmed to be anhydrous by elemental analysis. All aqueous solutions were prepared using deionized and redistilled water. IR spectra were recorded on a Shimadzu FTIR-4200 spectrometer. ^{1}H NMR spectra were recorded on a JEOL Alpha (400 MHz) spectrometer. 3-(Trimethylsilyl)propionic-*2,2,3,3-d$_4$* acid sodium salt in D_2O and tetramethylsilane in DMSO-*d*$_6$ were used as internal references for ^{1}H and ^{13}C NMR measurements. The pD values in D_2O were corrected for a deuterium isotope effect using pD = [pH meter reading] + 0.40. Elemental analysis was performed on a Perkin-Elmer CHN analyzer 2400.

2:3 Supramolecular Complex of 9 and CA^{2-} (10·3(ClO_4^-)·3(NO_3^-)·6H_2O). **9**·6(NO_3^-)·3H_2O·0.5EtOH (300 mg, 0.24 mmol),[24] cyanuric acid (51 mg, 0.40 mmol), and $NaClO_4$ (50 mg, 0.41 mmol) were dissolved in H_2O, and the pH was adjusted to pH 10 by addition of aqueous NaOH. After slow evaporation in vacuo, colorless prisms of **10**·3(ClO_4^-)·3(NO_3^-)·6H_2O (180 mg, 57%) were obtained (mp >280 °C) (although we have not experienced the explosion of ClO_4 salts of zinc complexes, the standard warning of their hazards should be noted). IR (KBr pellet): 3426, 3281, 1651, 1597, 1466, 1385, 1143, 1094, 1020 cm^{-1}. ^{1}H NMR (D_2O): δ 2.48−2.54 (12H, m, C*H*$_2$ of cyclen rings), 2.64−2.83 (48H, m, C*H*$_2$ of cyclen rings), 2.94−3.08 (24H, m, C*H*$_2$ of cyclen rings), 3.15−3.25 (12H, m, C*H*$_2$ of cyclen rings), 3.80 (12H, s, ArC*H*$_2$), 6.81 (6H, s, Ar*H*). ^{13}C{^{1}H} NMR (D_2O): δ 43.11, 44.95, 45.62, 49.55, 55.65, 113.18, 134.17 (peaks of carbonyl carbons of CA^{2-} were not observed). Anal. Calcd for $C_{75}H_{147}N_{36}O_{36}Cl_3Zn_6$: C, 34.28; H, 5.64; N, 19.19. Found: C, 34.40; H, 5.62; N, 19.15.

4:4 Supramolecular Complex of 9 and CA^{3-} (15·12(NO_3^-)·40H_2O). **9**·6(NO_3^-)·3H_2O·0.5EtOH (94 mg, 0.07 mmol) and cyanuric acid (9 mg, 0.07 mmol) were dissolved in H_2O, and the pH was adjusted to pH 11.5 by addition of aqueous NaOH. A solution was concentrated slowly in vacuo for 1 week, and colorless prisms of **15**·12(NO_3^-)·40H_2O (73 mg, 77% yield) were obtained (mp >280 °C). IR (KBr pellet):

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[38] After **15** was dissolved in H_2O, the whole was evaporated and dried in vacuo. The ^{1}H NMR of the resulting powders in DMSO-*d*$_6$ showed three peaks corresponding to **9**, **10**, and **17**.

[39] The ^{13}C NMR peaks of carbonyl carbons of uncomplexed CA and CA^{3-} in **15** appeared at δ 149.8 and 166.9, respectively, suggesting that the Zn^{2+}−N^- coordination functions as an electron-withdrawing group to cause the decrease of the pK_a value of the third imide proton of CA in supercomplexes.

[40] Because NO_3^- and ClO_4^- were found between CA^{2-} moieties in **10** (Figure 2), we examined the interaction of **10** with inorganic anions by ^{1}H NMR in D_2O at pD 8.0 ± 0.1 and 35 °C. Among various anions tested, I^-, ClO_4^-, SCN^-, and N_3^- caused considerable downfield shifts of the Ar*H* peak without dissociation of **10** (NO_3^-, SO_4^{2-}, F^-, Cl^-, Br^-, and IO_3^- gave negligible effect on ^{1}H NMR of **10**). Assuming that these anions are independently recognized at the three recognition sites of **10**, log K_{app} values (K_{app} = [X^-−(BS**10**)]/[X^-][BS**10**], where X^- is an anion and BS**10** is each of the three binding sites of **10**) were determined to be 2.7 for I^-, 2.6 for ClO_4^-, 2.3 for SCN^-, and 2.4 for N_3^-, respectively, by calculating with the Benesi−Hildebrand method: Conners, K. A. *Binding Constants, The Measurement of Molecular Complex Stability*; John Wiley and Sons: New York, 1987. It was confirmed that I^-, ClO_4^-, SCN^-, and N_3^- had negligible effect on the ^{1}H NMR spectra of **9**. Similarly, **14** had an interaction with SCN^- with log K_{app} of 2.2 under the same condition.

3440, 3280, 2944, 2880, 1541, 1441, 1385, 1098, 959 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 2.38−2.87 (192H, m, CH_2 of cyclen rings), 3.50 (24H, br s, ArCH_2), 3.82 (12H, br s, NH), 4.21 (24H, br s, NH), 7.08 (12H, s, ArH). ^{13}C{^{1}H} NMR (DMSO-d_6): δ 41.94, 43.66, 44.26, 48.80, 54.10, 131.85, 132.78, 166.92. Anal. Calcd for $C_{144}H_{344}N_{72}O_{88}Zn_{12}$: C, 32.77; H, 6.57; N, 19.11. Found: C, 32.76; H,6.56; N, 19.22.

Crystallographic Study of 10·3(ClO$_4^-$)·3(NO$_3^-$)·6H$_2$O. A colorless prismatic crystal of **9**·3(ClO$_4^-$)·3(NO$_3^-$)·6H$_2$O ($C_{75}H_{147}N_{36}O_{36}Cl_3Zn_6$, $M_r = 2627.84$) having approximate dimensions of 0.15 × 0.15 × 0.10 mm was sealed in a glass capillary. All measurements were made on a Rigaku Raxis IV imaging plate area detector with graphite-monochromated Mo Kα radiation. Indexing was performed from three oscillations which were exposed for 4.0 min. The crystal-to-detector distance was 125.00 mm with the detector at the zero swing position. Readout was performed in the 0.100 mm pixel mode. Cell constants and an orientation matrix for data collection corresponded to a primitive monoclinic cell with the following dimension: $a = 27.327(3)$ Å, $b = 29.127(2)$ Å, $c = 16.025(2)$ Å, $\beta = 90.56(1)°$, and $V = 12754(1)$ Å^3. The data were collected at a temperature of 25 ± 1 °C to a maximum 2θ value of 50.6°. For $Z = 4$ and $M_r = 2627.84$, the calculated density (D_{calcd}) was 1.368 g·cm^{-3}. The systematic absence of $h01$, $h + 1 \neq 2n$; $0k0$, $k \neq 2n$, uniquely determines the space group to be $P2_1/n$ (No. 14). A total of 60 3.00° oscillation images were collected, each being exposed for 20.0 min. A total of 19611 reflections was collected. The linear absorption coefficient, μ, for Mo Kα radiation is 12.6 cm^{-1}. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR 92) and expanded by means of Fourier techniques (DIRDIF 94). Three perchlorate, three nitrate ions, and six water molecules are contained in an asymmetric unit. The two nitrate ions, N36a and N37a, are disordered in the two locations around inversion centers of the crystal. The cyclen portions of the Zn complex ions and the nitrate ions were refined as rigid groups. Hydrogen atoms, excluding those of the cyclen carbons and water molecules, were included but not refined. The final cycle of full matrix least-squares refinement was based on 7240 observed reflections ($I > 3.00\sigma(I)$) and 773 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of, R ($= \sum||F_o| - |F_c||/\sum|F_o|$) = 0.091. $R_w = ((\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{0.5}) = 0.110$. The standard deviation of an observation of unit weight was 1.78. The weighting scheme was based on counting statistics and included a factor ($p = 0.082$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.24 and −0.66 e^-·Å^{-3}, respectively. All calculations were performed with the teXsan crystal structure analysis package developed by Molecular Structure Corp. (1992, 1994).

Crystallographic Study of 15·12(NO$_3^-$)·40H$_2$O. A colorless prismatic crystal of **15**·12(NO$_3^-$)·40H$_2$O ($C_{144}H_{344}N_{72}O_{88}Zn_{12}$, $M_r = 5277.29$) having approximate dimensions of 0.30 × 0.10 × 0.10 mm was sealed in a glass capillary and used for data collection. All measurements were made on a Rigaku Raxis IV imaging plate area detector with graphite-monochromated Mo Kα radiation. Indexing was performed from three oscillation which were exposed for 4.0 min. Cell constants and an orientation matrix for data collection corresponded to an I-centered cubic cell (Laue class, $m\bar{3}m$) with the following dimensions: $a = 23.430(4)$ Å and $V = 12862(3)$ Å^3. For $Z = 2$ and $M_r = 5277.29$, the calculated density (D_{calcd}) was 1.362 g·cm^{-3}. On the basis of the systematic absence of hkl, $h + k + 1 \neq 2n$ packing consideration, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be: $I\bar{4}3m$ (No. 217). The data were collected at a temperature of 25 ± 1 °C to a maximum 2θ value of 54.8°. A total of 16 3.00° oscillation images were collected, each being exposed for 20.0 min. The crystal-to-detector distance was 105.0 mm with the detector at the zero swing position. Readout was performed in the 100 μm pixel mode. Of the 2285 reflections collected, 1337 were unique ($R_{\text{int}} = 0.014$); equivalent reflections were merged. The linear absorption coefficient, μ, for Mo Kα radiation is 11.8 cm^{-1}. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient, 1.385 00e^{-7}). The structure was solved by direct methods (SIR 92) and expanded by means of Fourier techniques (DIRDIF 94). The cyclen portion was refined isotropically as a rigid group. The nitrate ions, except N31−O32, were located but not refined. Hydrogen atoms were not located. The final cycle of full matrix least-squares refinement was based on 1004 observed reflections ($I > 3.00\sigma(I)$) and 76 variable parameter and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of R ($= \sum||F_o| - |F_c||/\sum|F_o|$) = 0.068. $R_w = ((\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{0.5}) = 0.086$. The standard deviation of an observation of unit weight was 1.62. The weighting scheme was based on counting statistics and included a factor ($p = 0.082$) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, sin θ/λ and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.43 and −0.39 e^-·Å^{-3}, respectively. All calculations were performed with the teXsan crystal structure analysis package developed by Molecular Structure Corp. (1992, 1994).

Potentiometric pH Titrations. The preparation of the test solutions and the calibration method of the electrode system (Orion Research expandable ion analyzer EA920 and Orion Research Ross combination pH electrode 8102BN) were described earlier.[21−24] All the test solutions (50 mL) were kept under an argon (>99.999% purity) atmosphere. The potentiometric pH titrations were carried out with $I = 0.10$ (NaNO$_3$) at 25.0 ± 0.1 °C, and at least two independent titrations were performed. Deprotonation constants of Zn^{2+}-bound water K'_2 (= [HO$^-$-bound species][H$^+$]/[H$_2$O-bound species] and apparent affinity constants K_{app} = [(Zn$_3$L^3)$_2$−(CA^{2-} (or Bar^{2-}))$_3$]/[uncomplexed Zn$_3$L^3]$_2$[uncomplexed CA (or Bar)]$_3$ (M^{-4}), where CA is cyanuric acid and Bar is barbital) were determined by means of the program BEST.[30] All the σ fit values defined in the program are smaller than 0.03. The K_W (= a_{H^+}·a_{OH^-}), K'_W (= [H$^+$][OH$^-$]) and f_{H^+} values used at 25 °C are $10^{-14.00}$, $10^{-13.79}$, and 0.825. The corresponding mixed constants, K_2 (= [HO$^-$-bound species]a_{H^+}/[H$_2$O-bound species]), are derived using [H$^+$] = a_{H^+}/f_{H^+}. The species distribution values (%) against pH (= −log[H$^+$] + 0.084) were obtained using the program SPE.[30]

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Supporting Information Available: ORTEP drawing, selected bond lengths, selected lengths of the intramolecular hydrogen bonds, selected bond angles of **10** are listed in Supporting Information. Stick drawing, selected bond lengths, and selected bond angles of **15** are also included in Supporting Information Available. Tables include crystallographic parameters, atomic coordinates, equivalent isotropic temperature factors, anisotropic temperature factors, bond distances, and bond angles in CIF format for **10**·3(ClO$_4^-$)·3(NO$_3^-$)·6H$_2$O and **15**·12(NO$_3^-$)·40H$_2$O (print/PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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